7 Pseudopotentials

7.1 Introduction

Heavy elements are the nightmare of theoreticians.

- Many electrons
- Many orbitals
- Relativistic dynamics

Solution: Find a *pseudopotential* with a ground state which is the lowest needed valence orbital.

- **Local PP** (the same for all values of l)
- **Semi-local PP** (different radial part for different values of l):,

$$V_l = \mathcal{P}_l V_l(r) \mathcal{P}_l, \tag{7.1}$$

$$\mathcal{P}_l = \sum_{m=-l}^{l} |lm\rangle\langle lm|. \tag{7.2}$$

Works.

7.2 A bit of history

- **H. Hellmann**, "Quantenchemie" (1937), p. 111– . The *Zusatzpotential* for alkali metals

$$U(r) = -\frac{1}{r} + \frac{A}{r} \mathrm{e}^{-2\kappa r} \tag{7.3}$$

- **P. Gombás**, *Z. Phys.* **94** (1935) (?) 473,479.
"Pseudopotentiale", Springer, Wien (1967).
"Ein Besetzungsverbotpotential".

- A historical wandering: **Phillips-Kleinman**, Phys. Rev. **116** (1959) 287.

$$(T + V)\psi_i = \varepsilon_i \psi_i, \tag{7.4}$$

$$V(r) = \frac{(\varepsilon_i - T)\psi_i(r)}{\psi_i(r)}. \tag{7.5}$$

Right ε_i, wrong norm of ψ.

- Fix: **shape-consistent PP**, **norm-conserving PP**. A discussion about which term was in use first is reproduced in figure (7.1) (P. Pyykkö, private communication to **R. Nieminen**, May 13, 1994).

- An own pseudo-potential for the spin-orbit interaction:

$$V^{\mathrm{SO}}(r) = \sum_{l=1}^{l_{\max}} \frac{2\Delta V_l(r)}{2l+1} \mathcal{P}_l \underline{l} \cdot \underline{s} \mathcal{P}_l. \tag{7.6}$$

$$\Delta V_l(r) = V_{l,l+\frac{1}{2}}(r) - V_{l-\frac{1}{2}}(r) \tag{7.7}$$

$$= \sum_k \Delta A_{lk} \mathrm{e}^{-a_{lk} r^2} \tag{7.8}$$

P.A. Christiansen, **Y.S. Lee**, **K.S. Pizer** *J. Chem. Phys.* **71** (1979) 4445.
P. Hafner, **W.H.E. Schwarz** *Chem. Phys. Lett.* **65** (1979) 537.

- The electric polarizability of the ionic core, and the core-valence correlation energy.

$$V_{\mathrm{CPP}} = -\frac{1}{2} \sum_\lambda \alpha_\lambda (\bar{f}_\lambda)^2 \tag{7.9}$$

Here α_λ is the polarizability of core λ and $\bar{f}_\lambda$ the electric field seen by the core λ.
P. Fuentealba, Thesis, Stuttgart (1984)
W. Müller, **J. Flesch**, **W. Meyer**, *J. Chem. Phys.* **80** (1984) 3297, 3311.

7.3 Where to get pseudopotentials

- **USA**:
  - K.S. Pitzer
  - Los Alamos (Hay & Wadt)
  - P.A. Christiansen
  - W. Ermler
  - W.J. Stevens (ECP=PP)
- **Canada, Sweden, Spain**: Huzinaga, Wahlgren, nodal model potentials.
- **Germany**: Stuttgart (Dolg, Stoll, Schwerdtfeger, ...) "Energy consistent PP".

  `www.theochem.uni-stuttgart.de`
- **France**: Toulouse (Daudley, Teichteil, ...)

F: pyykko@cc.helsinki.fi
T: rnieminen@csc.fi
D: 13 May, 1994
S: History of pseudopotentials

Dear Risto,

As you may recall we had some time ago a friendly
"who was first" discussion on the history of the
"shape-consistent" or "norm-conserving" pseudopotentials.
The former name is used in chemistry and the latter in physics;
the common feature of both is that the pseudo wave function
reproduce the full wave function in the valence region. (i)

At the workshop of Pseudopotentials of the REHE
programme of ESF in Toulouse on
Monday, I asked the members of the conference how they thought
that these ideas were originally developed.

Apparently the first article was /1/ in 1975. The idea (i) is
clearly stated in Fig. 2 and pp. 288-.

According to Walter Ermler, who was at Berkeley in the late
1970'ies, there was communication between the chemists, like him
and the physicists, like Dr. A. Zunger, working with M. Cohen.
Anecdotally, "we were rather shouting at each other than
collaborating", though.

The first paper from Berkeley/Chemistry seems to be /2/. It quotes /1/.
The Acknowledgement of /2/ thanks A. Zunger for a preprint of /3/,
"in the revision to final form of this manuscript", and
also L. Kahn for private communications on his work.
Thus the first papers /2, 3/
and the Physics and Chemistry efforts indeed seem entirely parallel.
None of the papers /1-3/ uses any particular name for the idea.

In his review /4/ Kahn quotes for the 'shape-consistent'
idea (i), his eq. (33), also /5, 6/. Kahn et al. /7/ also clearly
discuss the idea (i) in their II.B.ii, without quoting /1/.

Hamann et al. /6/ have the title 'Norm-conserving pseudopotentials'
and quote /3, 5/ but not /1, 7/.

Conclusion: The work in the references /1, 7 5/ seems to preceed
that in ref. /3, 6/. The name 'norm-conserving' form 1979 may be
older than the name 'shape-consistent', whose exact origin I have not
found. I believe that it was used in the Los Alamos workshop on the
subject in 1981.

1. Ph. Durand and J.-C. Barthelat, Theor. Chim. Acta 38 (1975) 283-202.
2. P.A. Christiansen, Y.S. Lee and K.S. Pitzer, J. Chem. Phys. 71 (1979)
   4445-4450.
3. A. Zunger, J. Vac. Sci. Technol. 16 (1979) 1337-1438.
4. L. Kahn, Int. J. Quantum Chem. 25 (1984) 149-183.
5. A. Redondo, W.A. Goddard III and T.C. McGill, Phys. Rev. B 15 (1977)
   5038-5048. Check ref. 6-7 there.
6. D. R. Hamann, M. Schlueter and C. Chiang, Phys. Rev. Letters 43 (1979)
   1494-1497.
7. L.R. Kahn, P. Baybutt and D.G. Truhlar, J. Chem. Phys. 65 (1976) 3826-
   3853.

Figure 7.1: e-mail, May 13, 1994